Rate of Penetration of a Fluid into a Porous Body

II. Verification of the Generalization of the Washburn Equation, for Organic Liquids in Glass Capillaries [1]

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The rate of penetration of a liquid hydrocarbon or an alcohol into a glass capillary is more rapid if the capillary has been outgassed, than if its surface is covered with a duplex film of the liquid. The increase in rate is as large as 10%. If the pore walls are covered by an adsorbed film, the thickness of which is comparable to the pore radius, this leads to an accelerated rate of penetration in comparison to systems in which the pore radii are large. In the systems studied, there was a notable difference between hydrocarbons and octyl alcohol, which appeared when the glass was outgassed at 200°C under vacuum.

INTRODUCTION

It was recently shown (1, 2) that, for the penetration of a fluid into cylindrical pores of radius r, if the pore surfaces are initially not covered with an equilibrium adsorbed film of the penetrating liquid, then the rate of penetration can be faster than that predicted by the Washburn equation (3, 4, 5). In the absence of gravity,

$$\frac{r\gamma_{lv}\cos\theta_Y}{2\eta} \leq \frac{d(x^2)}{dt} \leq \frac{r}{2\eta}$$
$$\times (\gamma_{lv}\cos\theta_Y + \pi_e - \pi_0). \quad [1]$$

Here, x is distance penetrated, γ_{lv} is the liquid–vapor surface tension, η is the viscosity, θ_Y is the equilibrium contact angle, and π is the spreading pressure:

$$\pi_e \equiv \gamma_s - \gamma_{sv}, \quad [2]$$

$$\pi_0 \equiv \gamma_s - \gamma_{s(t=0)}, \quad [3]$$

where γ_s is the surface free energy of the solid in the absence of adsorption of molecules of the penetrating liquid, γ_{sv} is the solid surface free energy in equilibrium with the saturated vapor, and $\gamma_{s(t=0)}$ is the solid surface free energy at zero time; $\gamma_s \geqq \gamma_{s(t=0)} \geqq \gamma_{sv}$. For the systems reported in this paper, the advancing contact angle was indistinguishable from zero. Setting $\theta_Y = 0$, we write

$$\frac{r\gamma_{lv}}{2\eta} \leq \frac{d(x^2)}{dt} \leq \frac{r}{2\eta}(\gamma_{lv} + \pi_e - \pi_0)$$
$$= \frac{r}{2\eta}(\gamma_{s(t=0)} - \gamma_{sl}). \quad [4]$$

The left equality (which is the Washburn equation) holds provided that the solid surface is covered with a duplex film of the penetrating liquid, or that dissipative transport mechanisms maintain such a film, advancing well ahead

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of the liquid front. An example of a dissipative transport mechanism, which in many cases may proceed rapidly enough to maintain such a film, is evaporation from the liquid, followed by diffusion or flow down a pore, and finally, adsorption or condensation on the walls of the pore. The left relation holds as an inequality if the additional free energy, associated with the wetting of the solid in the absence of a duplex film, can contribute in a nondissipative manner to the *effectual* driving force for flow. The free energy change during flow of a liquid into a cylindrical tube may be identified as the free energy of immersion [6]: If the walls are covered with a film that is in equilibrium with the saturated vapor, we have

$$\Delta G^{i(\text{sat})} = \gamma_{sv} - \gamma_{sl}. \qquad [5]$$

If the walls are devoid of adsorbed film, we have

$$\Delta G^i = \gamma_s - \gamma_{sl}, \qquad [6]$$

$$\Delta G^i - \Delta G^{(i\text{sat})} = \pi_e. \qquad [7]$$

If the walls are initially covered with a film such that the surface free energy is $\gamma_{s(t=0)}$, the free energy change is given by

$$\Delta G^{i0} = \gamma_{s(t=0)} - \gamma_{sl}, \qquad [8]$$

$$\Delta G^i - \Delta G^{i0} = \pi_0. \qquad [9]$$

The purpose of this study was to establish whether appreciable deviations from the Washburn equation, as indicated by Eqs. [1] and [4], are observable.

THEORY

The following theoretical considerations, beyond those in (2), were developed for the purpose of testing the new equations.

It is quite general to assume that only a fraction, α, of the excess driving force, $\pi_e - \pi_0$ in Eqs. [1] and [4], is used in a nondissipative manner. Then, we can write Eq. [4] in the form

$$\frac{d(x^2)}{dt} = \frac{r[\gamma_{lv} + \alpha(\pi_e - \pi_0)]}{2\eta}, \qquad 0 \leq \alpha \leq 1. \qquad [10]$$

Since deviations from the Washburn equation have not been reported before, it is to be expected that α is commonly small. The maximum conceivable rate would be given by Eq. [10] with $\alpha = 1$.

We have set out to test these equations in perhaps the simplest possible system: vertical glass capillary tubes. Vertical orientation has an advantage over horizontal in that small deviations from horizontal can cause quite appreciable errors. For a vertical tube of radius r, the rate, when the meniscus is at height x above the liquid surface, is given by:

$$\frac{dx}{dt} = \frac{r^2}{8\eta x} \left\{ \frac{2[\gamma_{lv} + \alpha(\pi_e - \pi_0)]}{r} - \rho g x \right\}, \qquad [11]$$

where ρ is the density of the fluid.

Integrating Eq. [11] between elevations x_1 and x_2, we obtain

$$
\begin{aligned}
t_p &= t_2 - t_1 \\
&= \frac{8\eta}{\rho g r^2} \left[\frac{2[\gamma_{lv} + \alpha(\pi_e - \pi_0)]}{\rho g r} \right. \\
&\quad \times \ln \left\{ \frac{2[\gamma_{lv} + \alpha(\pi_e - \pi_0)]/\rho g r - x_1}{2[\gamma_{lv} + \alpha(\pi_e - \pi_0)]/\rho g r - x_2} \right\} \\
&\quad \left. - (x_2 - x_1) \right]. \qquad [12]
\end{aligned}
$$

The thickness, δ, of the film on the solid is a variable that was found to be important. It may be assumed that there is some limiting thickness, δ_d for a duplex film, such that for $\delta < \delta_d$, the vapor pressure of the adsorbed film is appreciably less than the saturation pressure p_0; and for $\delta > \delta_d$, the vapor pressure is not experimentally different from p_0. We consider, here, only capillary or pore radii in the range large enough that Kelvin equation corrections to the vapor pressure need not be taken into account. For clarity of the qualitative argument regarding δ, we discuss only a horizontal tube (see Fig. 1).

If δ_d is comparable to the radius r, then at saturation, the effective radius will be $r - \delta_d$, with respect to the driving force for pene-
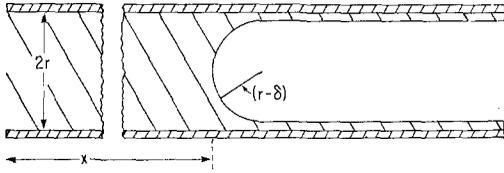
FIGURE 1

tration:

$$\Delta p = \frac{1}{\pi(r - \delta_d)^2} \frac{\partial G}{\partial x} = \frac{2\gamma_{lv}}{r - \delta_d}. \quad [13]$$

The viscous drag, however, will be that of a column of liquid, of length x, in a tube whose radius is r

$$\Delta p_{\text{drag}} = \frac{8\eta x}{r^2} \frac{dx}{dt}. \quad [14]$$

Equating Δp to Δp_{drag}, we obtain for a saturated system,

$$\frac{d(x^2)}{dt} = \frac{r^2\gamma_{lv}}{2(r - \delta_d)\eta}. \quad [15]$$

If $\delta < \delta_d$, $\pi_e - \pi_0 > 0$, and γ_{lv} must be replaced by $\gamma_{lv} + \alpha(\pi_e - \pi_0)$.

Then, the most general relation for a horizontal tube is,

$$\frac{d(x^2)}{dt} = \frac{r^2[\gamma_{lv} + \alpha(\pi_e - \pi_0)]}{2(r - \delta)\eta}. \quad [16]$$

A corresponding relation can be written for a vertical tube. From Eq. [16], we see that the penetration time between two elevations (see Eq. [12]) will be related to the amount adsorbed through three parameters: δ, $(\pi_e - \pi_0)$, and α. The dependence of α on δ is not at present readily accessible; but it might be expected that as $\delta \rightarrow \delta_d$, α could approach zero on account of surface diffusion and flow. Such a possibility would not interfere with studies such as those reported below, in which α was assumed independent of δ, because the only effect of such a decrease in α would be to relax the requirement of saturation of the solid surface, for runs with prewetted capillary walls.

If $\delta > \delta_d$, the film on the solid is, in effect, bulk liquid. The cylindrical configuration is stabilized by the flow of gas. It was found that, in clearing the liquid from a tube by sucking gas through it, if the gas flow was stopped too soon, biconcave lenses of liquid formed, blocking the tube. These arose because of the unstability of a film of bulk liquid on the inside of a cylinder (see Fig. 2). If the initial film is thin in relation to the tube radius, the process shown in Fig. 2 will go so slowly that even though $\delta > \delta_d$, the film is, in effect, stable.

The practical effect of large values of δ on the experiments could be predicted as follows: The data are reported as $\Delta t\%$, defined as

$$\Delta t\% = 100(1 - t_{pb}/t_{pw}), \quad [17]$$

where t_{pb} is the penetration for travel between levels x_1 and x_2, for a capillary that has been outgassed, and t_{pw} is the penetration time for the same capillary, the surface of which is covered by an adsorbed film whose thickness is δ. The film could be generated by drawing saturated vapor through a previously baked tube or (which was more generally used) starting with a tube that was full of the liquid, and draining it by drawing gas through it for a specified time. For a horizontal capillary, the integrated form of Eq. [16], in the case where
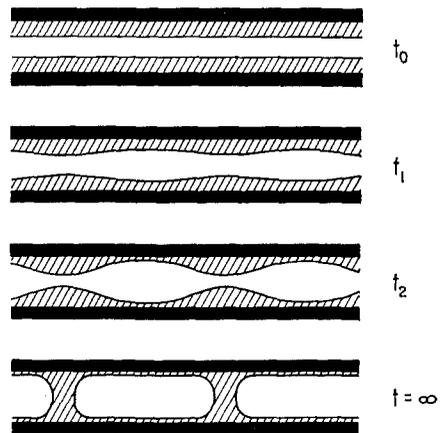

FIG. 2. Growth of unduloid unstabilities of a thick liquid film inside a capillary tube, after flow of gas has been stopped.

$x = 0$ when $t = 0$, is

$$t = \frac{2(r - \delta)\eta x^2}{r^2[\gamma_{lv} + \alpha(\pi_e - \pi_0)]}. \qquad [18]$$

Then, $\Delta t\%$ is given by

$$\Delta t\% = 100$$

$$\times \left\{ 1 - \frac{r[\gamma_{lv} + \alpha(\pi_e - \pi_0)_w)]}{(r - \delta)[\gamma_{lv} + \alpha(\pi_e - \pi_0)_b]} \right\}. \quad [19]$$

For δ comparable to r, and $\delta > \delta_d$, the quotient on the right is greater than 1, and $\Delta t\%$ will be negative. If $\delta_d \ll r$, then as $\delta \rightarrow \delta_d$, $\Delta t\%$ will approach a maximum. If the gas is saturated, $\Delta t\%$ will attain a constant value when $\delta = \delta_d$ and $\pi_0 = \pi_e$. If it is unsaturated, then, after the maximum of $\Delta t\%$, δ will decrease below δ_d, π_0 will decrease below π_e, and $(\pi_e - \pi_0)_w$ will increase, though staying smaller than $(\pi_e - \pi_0)_b$. The $\Delta t\%$ should then decrease; and this was, in fact, found to happen (see Results).

EXPERIMENTAL METHODS

Two series of experiments were carried out. In the first, the tubes were baked at 150° in air, for 6 to 10 hr, before the penetration measurements; the tubes were emptied between runs with suction from a water aspirator. In the second series, the outgassing was at 200°, in vacuum, and the suction was by vacuum pump. For both series, a preliminary set of measurements was made, varying the time of suction.

The liquids employed were spectro grade benzene (Eastman, and Fisher), spectro grade toluene (Eastman), n-octanol (Eastman, mp −15 to −16°C) and ACS reagent grade methanol (J. T. Baker). The advancing contact angle of these liquids on clean glass is indistinguishable from zero. An advancing contact angle of 3°C would lead to an increase of 0.25% in the penetration time under the conditions of this study. It would be expected that the advancing contact angle on prebaked glass would be equal to or greater than that on

presaturated glass, and consequently, that the penetration time for presaturated tubes would be equal to that with prebaked tubes, or larger, if contact angle effects were the only variables. The results reported below were that the penetration time was smaller with prebaked tubes, so we can conclude that the possibility of nonzero contact angle effects does not vitiate our qualitative conclusions.

Pyrex glass capillaries, of about 0.0017 cm radius, were obtained from the Corning Glass Company and cut into lengths of about 30 cm. For such tubes, the equilibrium capillary rise is about 40 cm, with benzene. Measurements were made between elevations 5 and 20 cm. in each tube, and the penetration times were in the range, 100 to 300 sec. Two stationary telemicroscopes were used to observe the penetration. The tube radii were essentially constant from end to end. Since we were interested only in the difference in penetration time for each tube, prebaked vs presaturated, there was no need to measure the tube radii. To minimize annealing effects, all tubes were first heated at 250°C for 10 hr and cooled slowly to room temperature. The expansion of glass that accompanies wetting (7, 8, 9) was measured and found to be less than 0.01%.

The measurements were made at 20 to 23°C, and corrected to 20°C by means of known temperature coefficients of viscosity, surface tension and density. The liquids were contained in essentially closed beakers, for penetration runs, the top of the beaker being covered with aluminum foil with a small hole in it. With an open beaker, the temperature of benzene in the beaker was found to reach a temperature about 2.5°C below the air temperature; with an enclosed beaker, the liquid came within 0.3°C of air temperature, after about 1 hr. Both liquid and air temperatures were measured for each run.

Each capillary was clamped in an exactly vertical orientation, and the liquid was raised until it just touched the bottom of the tube. The positions x_1 and x_2 were marked on each tube with tape, which served both to ensure that elevations x_1 and x_2 were reproducible

(relative to the liquid surface) and to improve the observation of the time when the liquid reached each mark.

The general procedure of a run was to measure the penetration time with a single capillary, first baking it as noted above, then measuring t_p with a liquid (e.g., benzene). Then, the liquid was cleared from the tube by suction, and t_p was measured again; this was repeated three or four times.

Figures 3 and 4 show the results of two of the preliminary sets of experiments that were carried out to determine the optimum conditions for establishing duplex films on the solid. In each case, a single capillary was outgassed, and the penetration time, t_b, was determined. Then, it was drained with suction of air (by aspirator or vacuum pump) for the time indicated on the graph, and the penetration time t_w was measured. This draining process was repeated, and $\Delta t\%$ was determined as a function of draining time. The results for each tube are relative to the value of t_b for that particular tube; so in Figs. 3 and 4, the curves were normalized by moving up or down so that the maximum $\Delta t\%$ coincided with the mean $\Delta t\%$ reported below in Table I.

Figure 3 shows the effect of draining time for benzene. As might be expected, the vacuum pump was more rapid and more effective: The transient negative value of $\Delta t\%$ passed earlier, the maximum occurred earlier, and
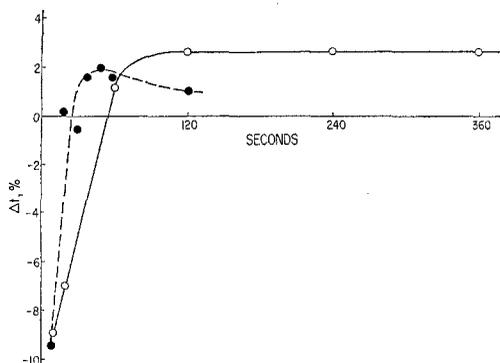

Fig. 3. Effect of suction time on benzene penetration rate. O, first series, with aspirator; ●, second series, with vacuum pump.
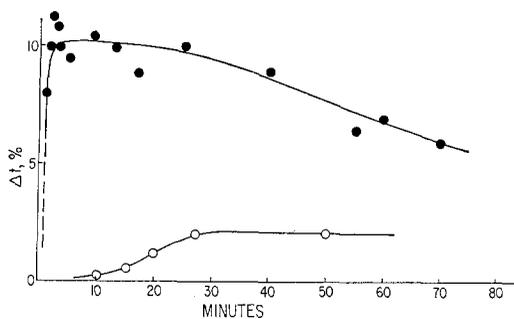

Fig. 4. Effect of suction time on n-octanol penetration rate. O, first series, with aspirator; ●, second series, with vacuum pump.

the expected decline with long times of passage of benzene-free air was in evidence. With the aspirator, a maximum $\Delta t\%$ was reached, but there was no subsequent decline, even for 60 min suction time. Toluene and methanol behaved quite similarly to benzene, with aspirator draining.

n-Octanol required a longer draining time than benzene, no doubt because of its lower vapor pressure and higher viscosity. An initial rise was observed, though no negative values of $\Delta t\%$. It may be seen that the two series differed both in the time required to reach maximum $\Delta t\%$ (just as with benzene) and (unlike benzene) in the height of the maximum. The latter effect will be discussed below.

A preliminary series was also run with methanol, starting with tubes baked at 150°C and saturating them by drawing methanol-saturated air through, with an aspirator, for 30 min. The results, expressed as $\Delta t\%$, differed by 0.36 ± 0.54 at 95% confidence level. Hence, the two methods of producing a duplex film did not have any statistically significant difference as regards penetration times.

RESULTS

Table I summarizes the results for the two series.

The statistical analysis of the data, Table I, is given with a very strict standard, the limits for 99.5% level of confidence. Had we chosen, say, the 90% confidence level, the $\pm$

TABLE I

Change of Penetration Time for Liquids, Prebaked versus Prewetted Pyrex Capillaries

Liquid	Aspiration or suction time (min)	Number of measurements	Mean $\Delta t\%$	Confidence limits for 99.5% confidence level
First series[a]				
Benzene	10	26	2.3	±0.4
Toluene	10	10	2.5	±0.5
Methanol	10	20	1.8	±0.4
n-Octanol	30	10	2.0	±0.4
Second series[b]				
Benzene	0.5 to 1	18	1.3	±0.6
n-Octanol	2 to 3	41	10.7	±4.6

[a] Baking at 150°C, 1 atm pressure. Drained by aspirator suction.

[b] Baking at 200°C in vacuum. Drained by suction with vacuum pump.

spread would have been narrower; e.g., in Table I, Second series, ±0.35 for benzene and ±2.8 for n-octanol. Employing another conservative statistical criterion, the "Student t test" [10], we can report with better than 99.5% confidence that the mean values of $\Delta t\%$ were, in every case, different from zero.

The results for benzene, under the two operating conditions, are not statistically distinguishable. The results with n-octanol are quite significantly different, no doubt on account of the stronger conditions of outgassing in the second series. It is possible that adsorbed water or n-octanol was not completely desorbed at 150°C and 1 atm pressure, and that this residual film decreased the surface free energy of the glass by a very considerable quantity. The aspirator also may have been a source of water.

DISCUSSION

We may conclude that the experimental evidence supports the theory proposed by Good (1, 2). The statistical analysis shows that, as a strictly empirical result, there is a significant anomaly, with respect to the Washburn equation. Had there been no explanation of this anomaly, it would have been necessary to seek one, because the results are well outside the limits of experimental error that are exhibited by the raw data. And in absolute

magnitude, the effects is not trivial: The value, of 10.7% for n-octanol (Table I, Second series) is in itself a notable magnitude. Moreover, the unexpected discovery of a difference in the behavior of the system, glass-n-octanol, for 200°C, vacuum outgassing, vs 150°C at 1 atm, is an empirical indication that the excess rate of penetration, above the level predicted by the Washburn equation, is an effect that has intrinsic significance. Since deviations from the Washburn equation were predicted, we can conclude that the theory of Good (1, 2) may be regarded as, at the least, corroborated.

The difference in behavior between n-octanol and benzene, in Table I, Second series, is probably related to the tendency of n-octanol to form an oriented adsorbed film, and to the lower vapor pressure of the liquid. Since the mean $\Delta t\%$ for methanol was nearly the same as for benzene and toluene, in the first series, the hydrogen bonding property of hydroxyls was apparently not the sole determining factor giving rise to this difference. The degree of outgassing of the solid, apparently, was also an important factor.

If we interpret the excess rate of penetration as being due to nonzero values of the quantity $\alpha(\pi_e - \pi_0)$, then, in the first series, the range for this quantity was 0.3–0.45 erg/cm^2, for all four liquids. In the second series, the value for

benzene was about 0.2 erg/cm^2, and for n-octanol, about 2 erg/cm^2. In assigning causal responsibility for the excess rate of penetration, as between α and $\pi_e - \pi_0$, the higher results for n-octanol in the second series would point to a variation in $\pi_e - \pi_0$. This question must be investigated further, however.

We may speculate as to the microscopic mechanism of the accelerated transport in outgassed porous bodies. It can probably be described in terms of the Marangoni effect, and the fact that a gradient of surface free energy must exist, as between the solid surface a few Å ahead of the bulk liquid (where the film is duplex if the contact angle is zero, and where the effective γ is γ_{lv}) and the region far ahead of the liquid, where the surface free energy is close to γ_s, and $\gamma_s \gg \gamma_{sv}$. If the gradient is steep, then Maragoni flow could well do useful work, converting surface energy to mechanical, kinetic energy of flow.

REFERENCES

1. GOOD, R. J., *Chem. Ind.* 600 (1971).
2. GOOD, R. J., *J. Colloid Interface Sci.* **42**, 473 (1973).
3. WASHBURN, E. D., *Phys. Rev.* **17**, 374 (1921).
4. RIDEAL, E. K., *Phil. Mag.* **44**, 1152 (1922).
5. ELEY, D. D. AND PEPPER, D. C., *Trans. Faraday Soc.* **42**, 697 (1946).
6. HARKINS, W. D., "The Physical Chemistry of Surface Films," Reinhold, New York, 1952.
7. BANGHAM, D. H. AND FAKHOURY, N., *J. Chem. Soc.* 1324 (1931).
8. BANGHAM, D. H. AND RAZOUK, R. I., *Trans. Faraday Soc.* **33**, 1459 (1937).
9. HILLER, K. H., *J. Appl. Phys.* **35**, 1622 (1964).
10. GUTTMAN, I., WILKES, S. C., AND HUNTER, J. S., "Introductory Engineering Statistics," 2nd ed., Wiley, New York, 1971.